# Department of Defense Environmental Data Quality Issues: *Is It Really Perchlorate?*


National Monitoring Conference

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# Topics

- Data Quality Issues Affecting Missions and Operations
- Perchlorate Testing
  - Current Status of Methods
  - Is It Really Perchlorate?
  - Emerging Technology
- Promoting Sound Science

# Perchlorate


# Natural and Anthropogenic Sources

- Chilean fertilizer deposits
- New Mexican potash
- Canadian potash
- Californian hanksiteh
- Bolivian playa crusts

- Rocket fuel
- Fireworks
- High explosives
- Flares
- Herbicides
- Automobile airbags
- Tracer munitions
- Detergents

# *Data Quality Issues Affect Mission and Operations*

## *DoD EDQW Charter, DUSD(ES) Sept. 1996:*

- Develop DoD policy on sampling, testing & data quality
- Identify Best Practices; standardize across DoD
- Coordinate responses to legislative & regulatory actions
- Represent DoD on environmental data quality Issues
- Respond to DoD IG reports

# *Data Quality Issues*
## *Prescriptive vs. Performance-Based Methods*

- Office of Water
  - Prescriptive methods
  - Promulgated (e.g. 40 CFR 136)
- Office of Solid Waster and Emergency Response
  - Performance Based Measurement System (PBMS)
  - SW-846 Methods Manual encourages method modification to meet project needs
  - Performance vs. test procedure oriented
  - Criteria describe data quality needs
- State Modifications to PBMS
  - Some states legislate SW-846 Methods as requirements
  - Performance-based method modifications are not allowed

# *Data Quality Issues*
## *Example: Perchlorate*

- Unregulated Contaminant Monitoring Rule (UCMR) List 1 constituent
- Health effects controversial
- Currently 10 states (AZ, CA, FL, IL, MA, MD, NV, NM, NY, and TX) have health advisory limits (1-31 ppb)
- Increasing regulatory pressure to analyze for trace levels (low ppb, sub-ppb)
- Inadequate consideration for complex matrices, method limitations, and measurement uncertainty

# *Data Quality Issues*
## *DoD Interim Policy on Perchlorate, Sept 2003*

*Components must collect and compile perchlorate data for:*

- *Drinking water supplies* subject to Unregulated Contaminant Monitoring Rule (UCMR)
- *Wastewater discharges* permitted under National Pollutant Discharge Elimination System (NPDES)
- *Environmental restoration sites* where release may have occurred and complete human exposure pathway is likely to exist (IR)
- *Range assessments* conducted under Munitions Action Plan and Defense Planning Guidance

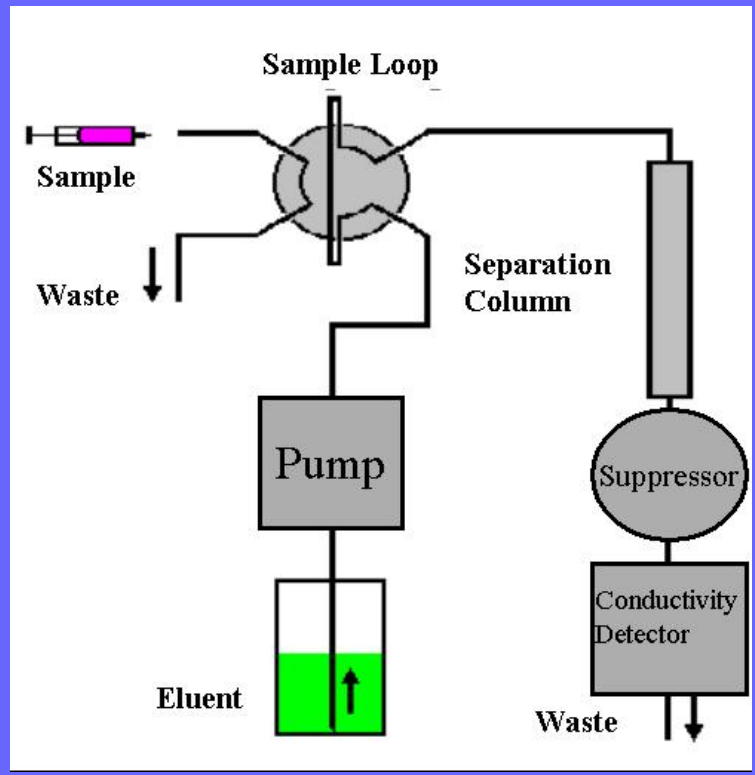
# *Perchlorate Testing*
## *Current Status of Methods*

- EPA Method 314.0
  - Ion Chromatography/conductivity detection
  - Drinking Water method
- SW-846 Method 9058 (Nov 2000 Draft)
  - IC/Conductivity detection (with suppressor)
- PBMS
  - Ion or Liquid Chromatography/Mass Spectrometry (IC or LC/MS)
  - IC or LC/MS/MS
  - Proprietary methods (Modified Method 8321a)

*No current, standardized method using MS*

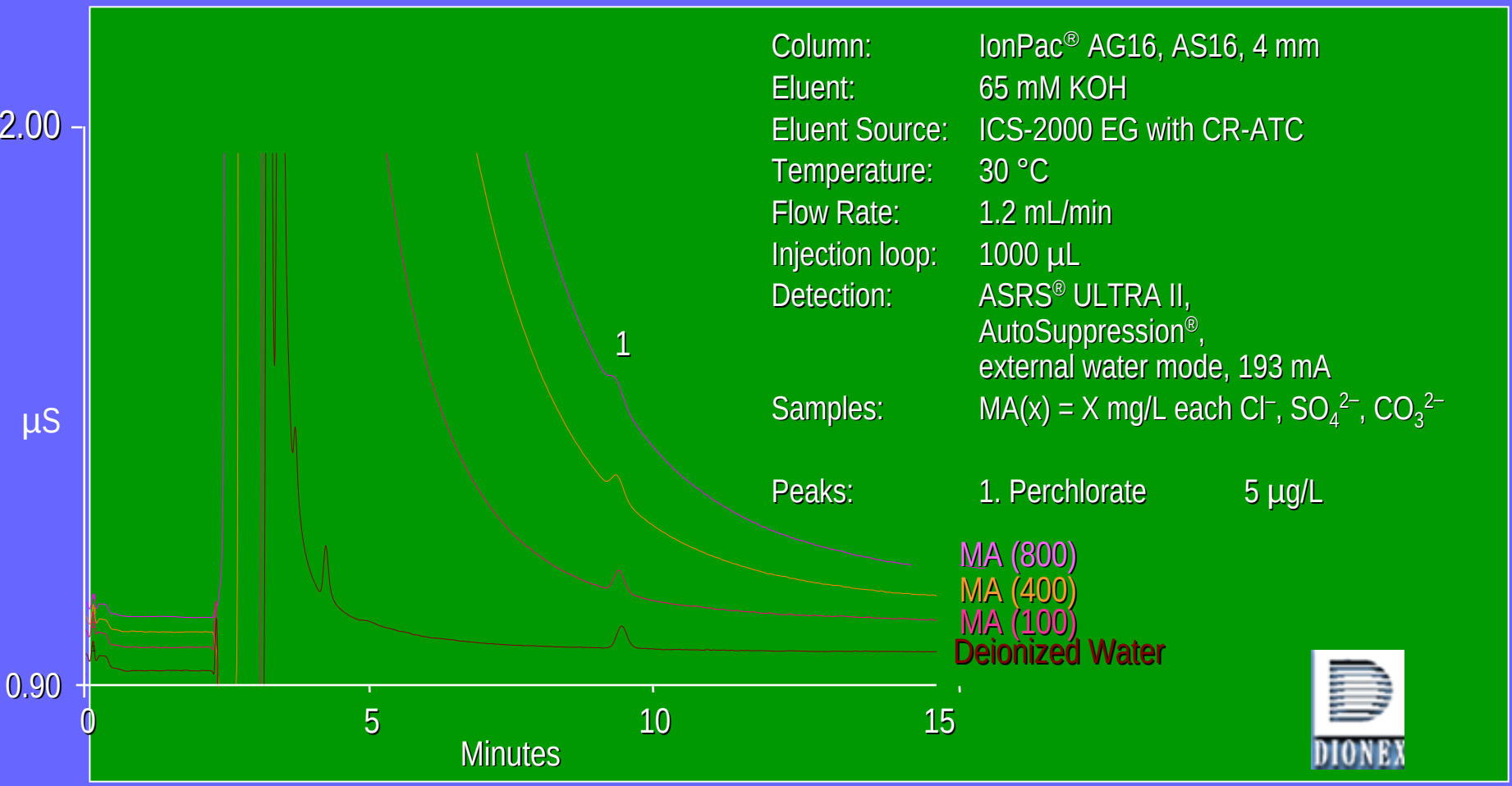
# *EPA Method 314.0*
## *Ion Chromatography/Conductivity*

- Currently the only EPA-approved method
- Method Reporting Level (MRL) = 4 ppb (deionized water)
- Compound identification based on ***retention time***
- Conductivity detector is non-specific
  - Responds to any substance that will conduct electric current



# EPA Method 314.0

## *Sensitivity decreases with increasing ionic strength*

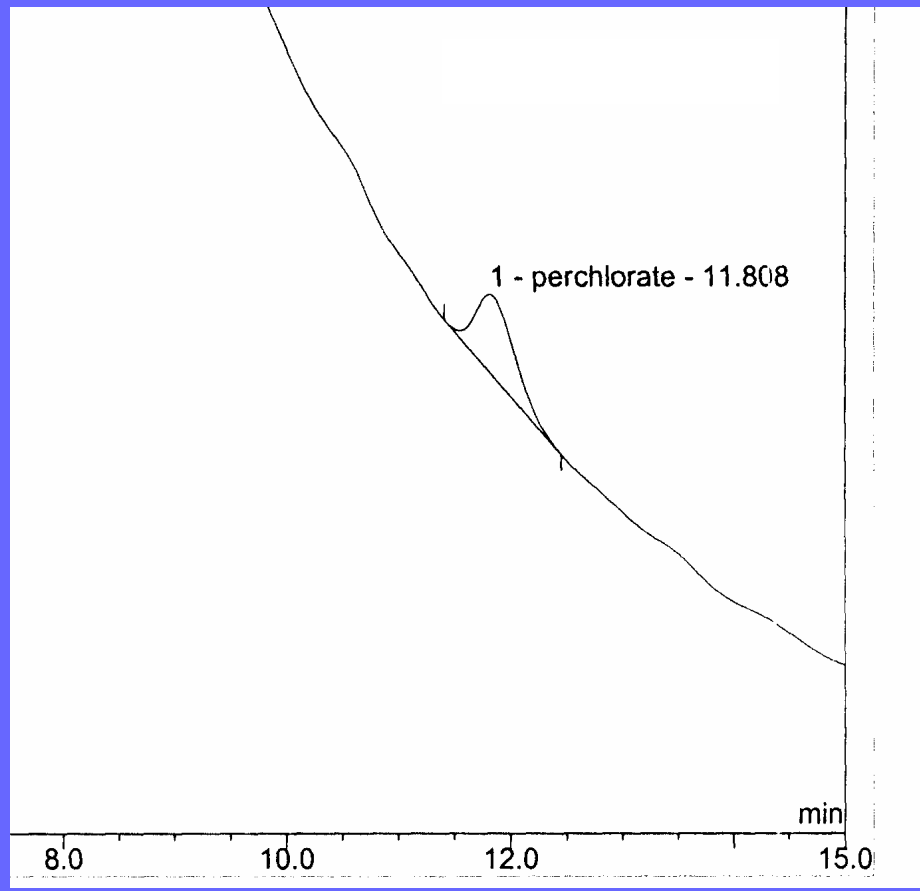



5 ppb perchlorate standard

# *Is it Really Perchlorate?*
## *Example #1*

- Treated rocket-motor wastewater, diluted 20X due to high conductivity
- Method 314.0 results: 670 ppb

  (Same result for 2 labs)
- LC/MS/MS results: non-detect

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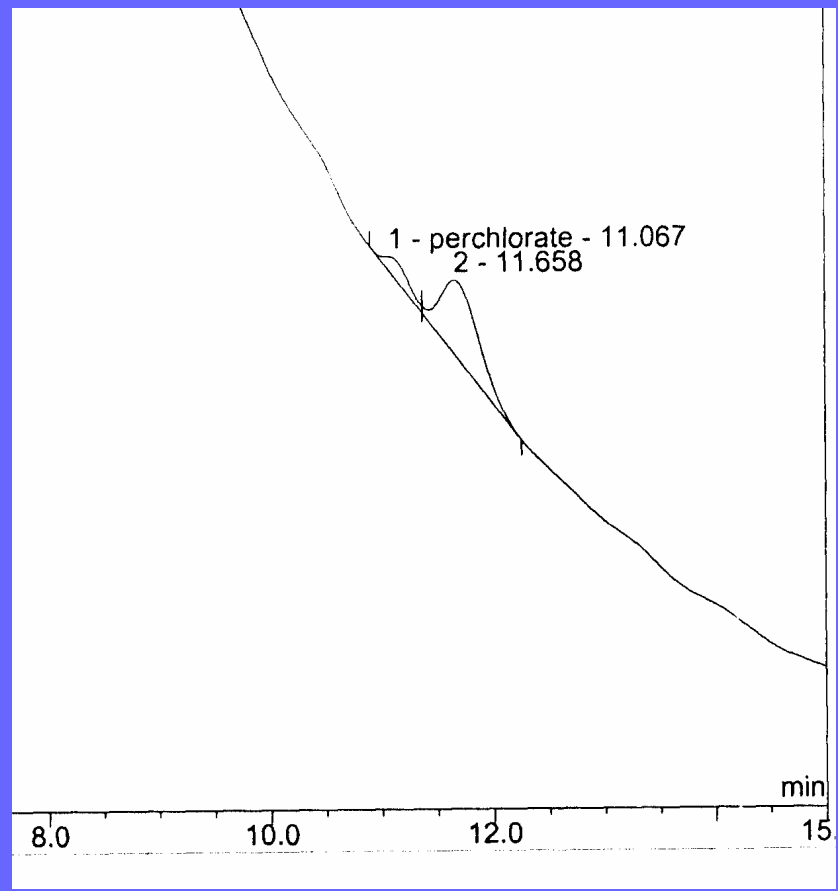
# *Is it Really Perchlorate*
## *Example #1 (cont'd)*

To check Method 314:

- 200 ppb perchlorate added to sample
- Spiked peak eluted with 0.6 minute retention-time shift
- Original peak due to interference, not perchlorate
- False positive occurred in every sample from site

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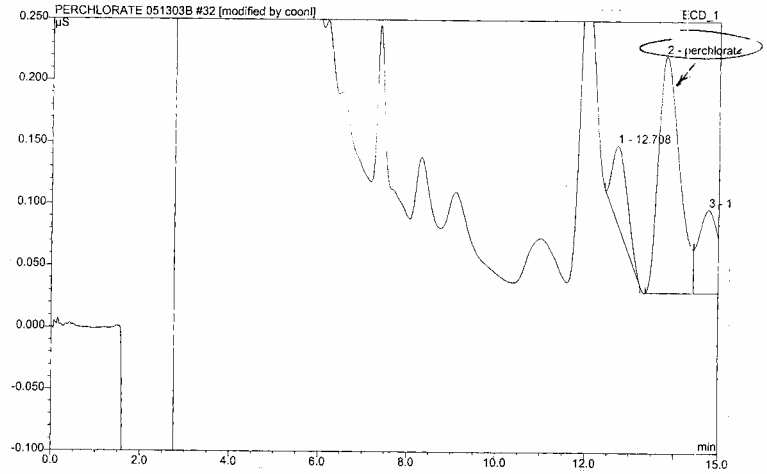
# *Is it Really Perchlorate?*
## *Example #2*

- Cooling tower water sample diluted 5X because of high conductivity
- Method 314.0 result: 194 ppb

**32 FM1FR D3E010357 -03 5X**

Sample D3E010357-03 5x dilution

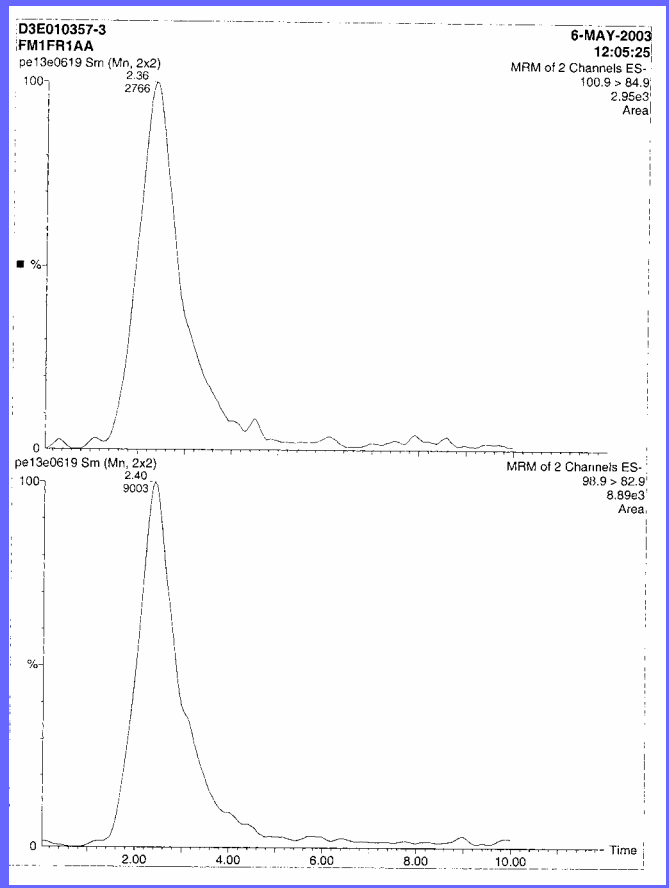
| | | | |
|---|---|---|---|
| *Sample Name:* | **FM1FR D3E010357 -03 5X** | *Injection Volume:* | **1000.0** |
| *Vial Number:* | **32** | *Channel:* | **ECD_1** |
| *Sample Type:* | **unknown** | *Wavelength:* | **n.a.** |
| *Control Program:* | **Perchlorate Program 11-19-02** | *Bandwidth:* | **n.a.** |
| *Quantif. Method:* | **IC5 Perch Low Quant Method 12-16-02** | *Dilution Factor:* | **5.0000** |
| *Recording Time:* | **5/14/2003 8:07** | *Sample Weight:* | **1.0000** |
| *Run Time (min):* | **15.00** | *Sample Amount:* | **1.0000** |




| No. | Ret.Time min | Peak Name | Height µS | Area µS*min | Rel.Area % | Amount ug/L | Type |
|---|---|---|---|---|---|---|---|
| 1 | 12.71 | n.a. | 0.062 | 0.026 | 15.87 | n.a. | BMB |
| 2 | 13.80 | perchlorate | 0.191 | 0.106 | 65.22 | 193.666 | BM * |
| 3 | 14.78 | n.a. | 0.067 | 0.031 | 18.91 | n.a. | M * |
| Total: | | | 0.321 | 0.162 | 100.00 | 193.666 | |

# *Is it Really Perchlorate?*
## *Example #2 (cont'd)*

- Undiluted sample analyzed by LC/MS/MS
- All four ions detected in proper 3:1 ratio
- LC/MS/MS result: 0.98 ppb



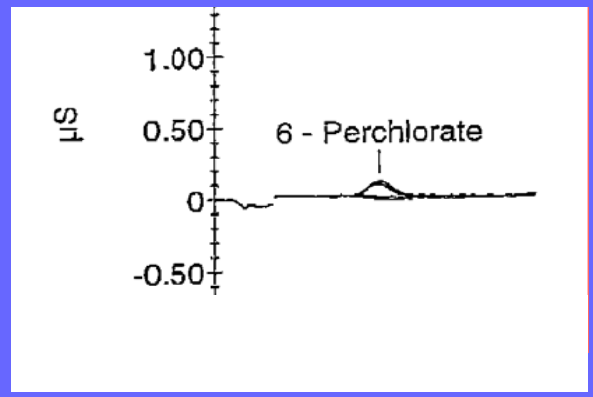
# *Is it Really Perchlorate?*
## *Example #3*

- Fluidized-bed reactor effluent from perchlorate remediation
- Matrix contains high organic and chloride concentrations
- Method 314.0 result: 220 ppb
- LC/MS/MS result: < 5 ppb
- Regulator now willing to accept LC/MS/MS

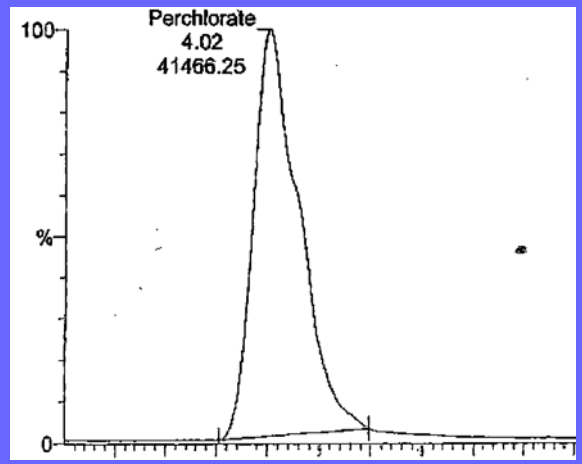
# *Is it Really Perchlorate?*
## *Example #4*

Groundwater Sample

Method 314.0 result: 15 ppb




IC/MS/MS result: 5.64 ppb



# *Emerging Technology*
## *October 2003 Perchlorate Testing Roundtable*

- Jointly sponsored by EDQW and IDQTF
- Held in conjunction with EPA Region 6 QA Conference (23 Oct 2003, Dallas)
- Convened technical experts (chemists) from:
  - DoD, EPA and other federal agencies
  - States
  - Academia
  - Analytical laboratories, instrument manufacturers

# *Emerging Technology*
## *Roundtable Objectives*

- Discuss current and developing technologies
- Identify most promising technologies
- Recommend path forward for method development

*Presentations and Summary can be viewed and downloaded*
www.navylabs.navy.mil

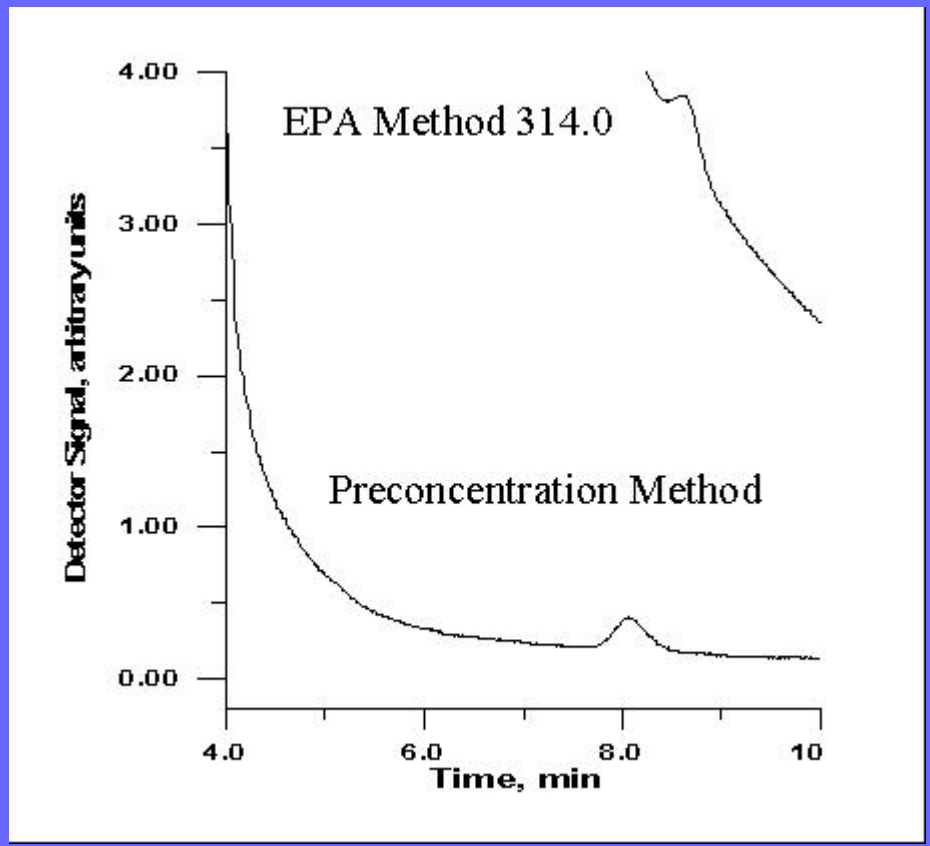
# *Emerging Technology*
## *Overview*

- ‘Improved’ Ion Chromatography (IC)
- Ion or Liquid Chromatography (IC or LC) with single or dual Mass Spectrometry (MS)
- Others
  - Ion-Selective Electrode (ISE)
  - Colorimetry
  - Capillary Electrophoresis
  - Ion Mobility/MS (FAIMS/MS)

# *Emerging Technology*
## *Improved Ion Chromatography*

- Preconcentration to improve sensitivity
- Pre-column sample cleanup to reduce ionic strength
- Dual column separation to reduce potential for false positives

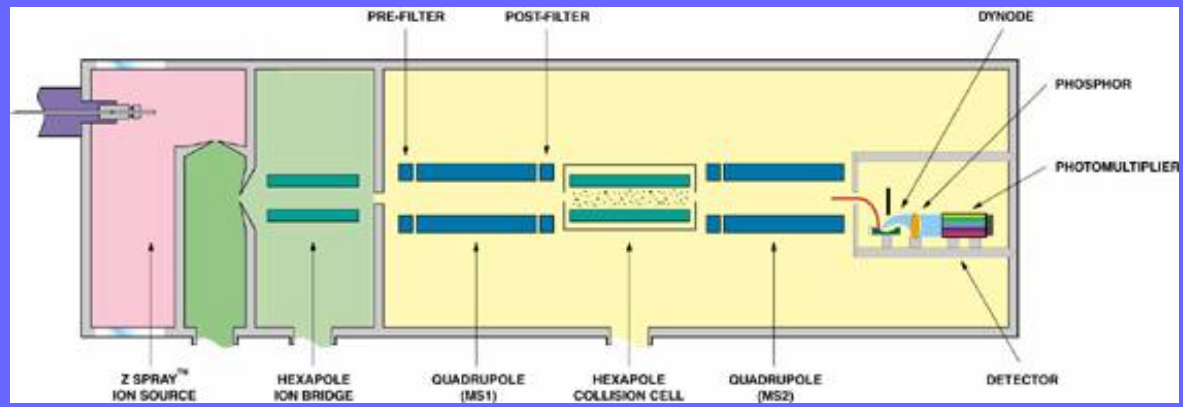
# *Emerging Technology*
## *Improved Ion Chromatography (cont'd)*



# *Emerging Technology*

## *IC or LC with single or dual Mass Spectrometer*

- IC separation & electrospray ionization
- First quadropole
  - MS monitoring 99 & 101 m/z
- Collision cell (loses an oxygen)
- Second quadropole
  - MS monitoring 83 & 85 m/z




Single MS monitors two ions and one mass ratio

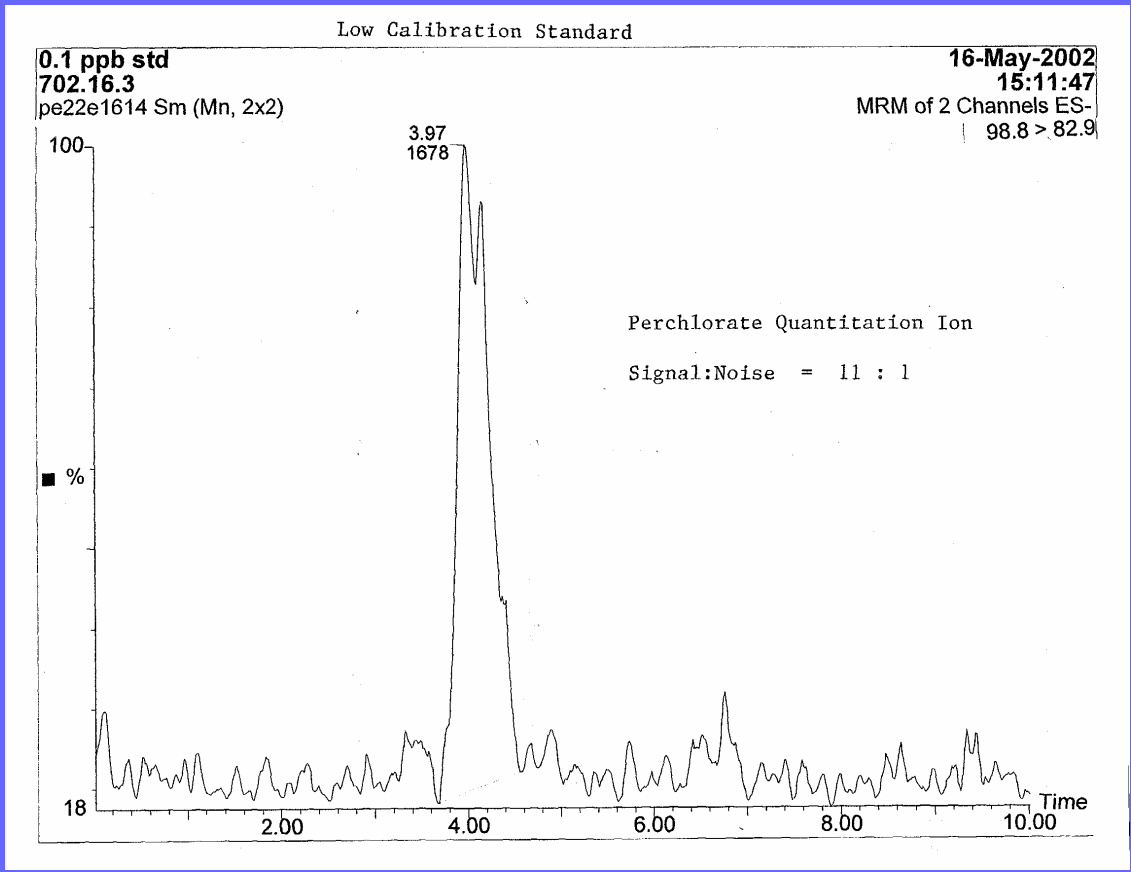
Dual MS monitors four ions and two mass ratios

(Check for 3:1 ion ratio)

# LC/MS/MS Sensitivity

## 0.1 ppb standard in DI water (m/z 83)

### calculated Method Detection Limit = 0.06ppb)

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# *Performance Summary*
## *IC or LC with Single or Dual MS*

- Greatly improved perchlorate selectivity and sensitivity
  - Positive identification of perchlorate ion
  - Higher confidence in low-level measurements
  - Sensitivity affected little by changes in ionic-strength (e.g., real world samples)
    - Water taken from the Great Salt Lake and diluted ten fold. Conductivity = 21000 µS MRL 2 ppb.
  - MRL of 0.2 ppb or lower
- Applicable to analysis of complex environmental matrices
- Commercially available as modified SW-846 Method 8321a

# *Method Performance Comparison*
## *Groundwater Samples*

| Performance Characteristics | Improved IC | IC or LC/MS | IC or LC/MS/MS |
|---|---|---|---|
| Approximate Working range | 1-40 ppb | 0.1-10 ppb | 0.1-10 ppb |
| MRL | 0.5 – 5 ppb* | 0.2 ppb | 0.2 ppb |
| Approximate Cost | $75 - $125 | $125 - $150 | $200 - $250 |

**dependent on matrix and type of improvement*

# *Promoting Sound Science*
## *Roundtable Summary*

- Proposed Method 9058 should not be finalized as written
- Method 314.0 modifications can improve sensitivity but not selectivity
- Positive results for perchlorate obtained using Method 314.0 should be confirmed using definitive technology (e.g. MS)

# *Promoting Sound Science*
## *Roundtable Next Steps*

- Provide comments on proposed SW-846 Method 9058 (complete)
- Facilitate process for development/approval of methods employing MS
- Characterize background occurrence of perchlorate
- Pursue development of DoD Guidance for sampling and testing of perchlorate
- Institutionalize the joint roundtable approach for technical problem-solving

# *Promoting Sound Science*
## *EDQW Interim Guidance for Perchlorate Testing*

Laboratory requirements:

- Quality systems conformance to DoD QSM
- Nationally-accepted accreditation
- Approval by one or more DoD Component(s)
- Matrix-specific proficiency-testing demonstration

# *Promoting Sound Science*
## *EDQW Interim Guidance for Perchlorate Testing*

Method requirements:

- Method Reporting Limit demonstration through analysis of a standard *at the MRL*
- MRL verification with each batch of samples
- Calibration and quality control that meet or exceed specifications of Method 314.0
- *Confirmation of non-specific results (i.e. Ion Chromatography) by definitive test methods*

# *Promoting Sound Science*
## *Perchlorate Testing Update*

*DoD:*

- EDQW Interim Sampling & Testing Guidance issued by DASN(E) Feb ‘04
- Perchlorate QAPP Handbook under development

*EPA/ORD & OGW/DW Methods to be finalized Summer ‘04*

- 314.1 – IC/Conductivity
  MRL – 0.5 ug/L
- 330.0 – IC/MS
  MRL – 0.2 ug/L
- 331.0 – LC/MS/MS
  MRL – 0.1 ug/L

# *The Payoff*

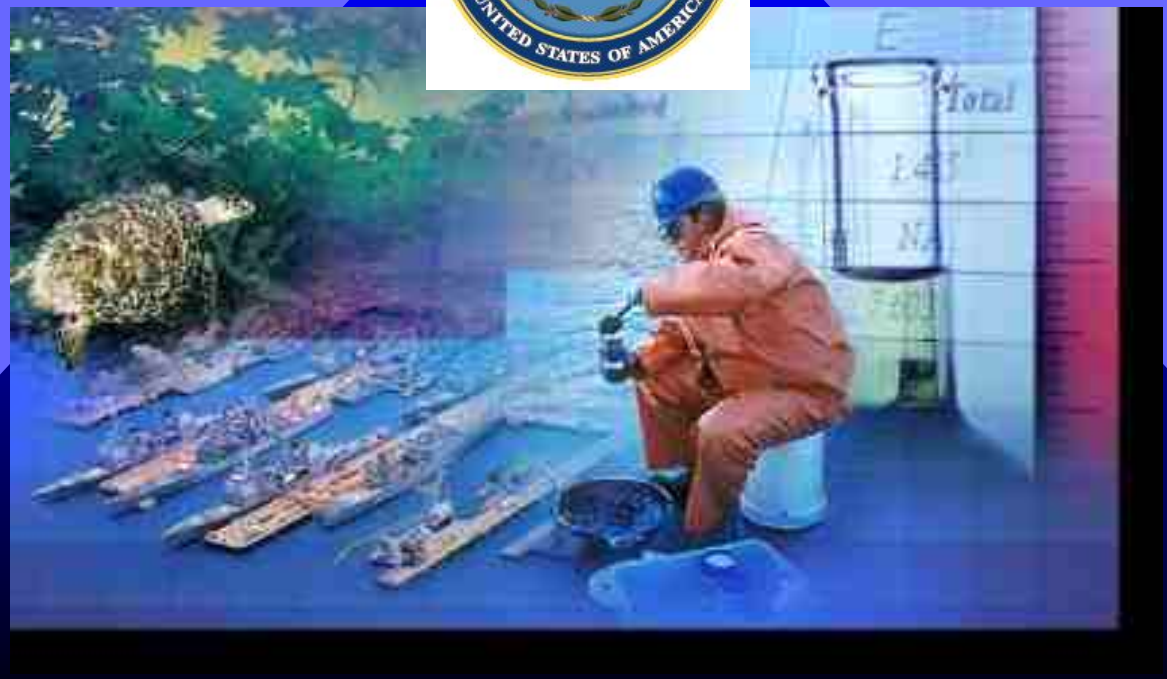
*Cost-effective data collection*

*Reproducible data*

*Sound environmental decisions*

# *Improving Environmental Data Quality*

*… Because the Right Decisions Require Quality Data*



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